

REMARKS

Favorable reconsideration and allowance of all pending claims in view of the following remarks is respectfully requested.

Claims 1-75 are pending in this application. The Examiner's indication in the Office Action that Claims 63-75 are allowed over the prior art is noted with appreciation.

The Examiner has rejected Claims 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 under 35 U.S.C. §102(b) as being anticipated by Price U.S. Patent No. 3,140,997 ("Price"). This rejection is respectfully traversed.

Price fails to disclose a stable colloidal suspension comprising "(a) a dispersed phase comprising *a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ...* and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, *wherein the stable colloidal suspension is substantially clear*" as generally recited in independent Claims 1, 18 and 43.

It is well established that for a prior art reference to evidence lack of novelty (anticipation) of the subject matter of a claim under 35 U.S.C. §102, each and every element as set forth in the claim must be either expressly or inherently described in a single prior art reference. *Verdegall Brothers, Inc. v. Union Oil Co. of Cal.*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir.), *cert. denied*, 484 U.S. 827 (1987).

In the Office Action, the Examiner states that "Price discloses compositions falling within the scope of "stable colloidal suspensions" having the instantly claimed components at column 1, lines 9-15 and 55-63, which acidic aqueous media is expected to form the instantly

claimed polymolybdates with the claimed molybdenum compounds and to hydrate said polymolybdates”.

In contrast to the presently claimed invention, Price discloses a process for preparing a colloidal molybdenum complex which involves extracting a *molybdenum compound* from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and removing the ketone and water from the dispersion. Price further discloses that the molybdenum compound is dissolved in a minimum amount of water necessary for a complete solution. Price goes on to state that sufficient mineral acid such as HCl is added to the solution to produce a solution having a normality of 2 to 12 and preferably 4 to 8. One skilled in the art of chemistry would readily understand that the pH of a solution having a normality of 2 to 12 and preferably 4 to 8, would be less than 2.

However, at a pH of less than 2, any polymolybdate present in the solution would necessarily breakdown into a non-polymeric molybdate. This is evidenced in, for example, Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264 (Exhibit 1) (as attached herein) which states that “The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo^{VI} from pH 7 down to 2. At pH 2 to 1 (depending on the concentration) break down of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as [Mo(OH)₆].” As such, the aqueous acidic solutions disclosed in Price would not contain (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more

dispersing agents and a diluent oil. In contrast, the aqueous acidic solutions would simply be an aqueous acidic solution containing a *molybdenum compound* in which the *molybdenum compound* is then extracted from the acidic aqueous solution with a ketone, dispersed in an oil-soluble basic metal-containing dispersant and the ketone and water are then removed from the dispersion. Accordingly, Price does not disclose a stable colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and (b) an oil phase comprising one or more dispersing agents and a diluent oil” as generally recited in independent Claims 1, 18 and 43.

In addition, Price further discloses in Example 2 that the dispersion is heated and stripped with gases to remove ketones and water. However, as stated in Example 4 of Applicants’ specification, extended dehydration of the recited colloidal suspension would provide a colloidal suspension which is hazy, i.e., not clear. Thus, Price would not even provide a substantially clear colloidal suspension much less a colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates and polyvanadates; and, (b) an oil phase comprising one or more dispersing agents and a diluent oil”, as presently recited in Claims 1, 18 and 43. Thus, Claims 1, 18 and 43 are further believed to not be anticipated by Price.

In addition, with respect to Claim 18, nowhere does Price disclose a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates,

polyvanadates, polyniobates, polytantalates, polyuranates, and mixtures thereof; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 18.

Nor, with respect to Claim 43, does Price disclose a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 43.

Rather, as stated above, Price discloses a colloidal molybdenum complex obtained by extracting a *molybdenum compound* from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and heating and stripping the dispersion with gases to remove the ketone and water from the dispersion. Price further discloses that “[a]fter a period of agitation for proper contact with the ketone and then a period of settling for separation, the ketone extract layer is added to a suitable dispersant.” Price goes on to state that the ketone and water are

thereafter removed. Certainly, then, Price further does not disclose all the element and limitations of the process set forth in Claim 18, comprising “mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates, polyvanadates, polyniobates, polytantalates, polyuranates, and mixtures thereof; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and, heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear.” Nor does Price further disclose all the element and limitations of the process set forth in Claim 43, comprising “mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and, heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear.” Accordingly, Claims 18 and 43 are believed to be further patentable over Price.

For the foregoing reasons, Claims 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 possess novel subject matter relative to Price. Thus, withdrawal of the rejection of 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 under 35 U.S.C. §102 (b) is respectfully requested.

The Examiner has rejected Claims 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 under 35 U.S.C. §103(a) as being obvious over Price. This rejection is respectfully traversed.

Price likewise provide no suggestion or motivation of a stable colloidal suspension comprising “(a) a dispersed phase comprising *a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ...* and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, *wherein the stable colloidal suspension is substantially clear*” as generally recited in independent Claims 1, 18 and 43.

Rather, as stated above, Price discloses a process for preparing a colloidal molybdenum complex which involves extracting a *molybdenum compound* from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and removing the ketone and water from the dispersion. Price further discloses that the molybdenum compound is dissolved in water and then sufficient mineral acid such as HCl is added to the solution to produce a solution having a normality of 2 to 12 and preferably 4 to 8. As stated above, one skilled in the art of chemistry would readily understand that the pH of a solution having a normality of 2 to 12 would be less than 2.

However, as stated above, at a pH of less than 2, any polymolybdate present in the solution would necessarily breakdown into a non-polymeric molybdate. This is again evidenced in, for example, Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264 (Exhibit 1) which states that “The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo^{VI} from pH 7 down to 2. At pH 2 to 1 (depending on the concentration) break down of polymers to give

dimeric and monomeric octahedral forms occurs, where the latter are often referred to as $[\text{Mo}(\text{OH})_6]$.” As such, the aqueous acidic solutions disclosed in Price would not contain (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents and a diluent oil. In contrast, the aqueous acidic solutions would simply be an aqueous acidic solution containing a *molybdenum compound* in which the *molybdenum compound* is then extracted from the acidic aqueous solution with a ketone, dispersed in an oil-soluble basic metal-containing dispersant and the ketone and water are then removed from the dispersion. Accordingly, one skilled in the art would be led away by the disclosure in Price.

In addition, Price further discloses in Example 2 that the dispersion is heated and stripped with gases to remove ketones and water. However, as stated in Example 4 of Applicants’ specification, extended dehydration of the recited colloidal suspension would provide a colloidal suspension which is hazy, i.e., not clear. Thus, nothing in Price would lead one skilled in the art to modify the colloidal molybdenum complex containing a dispersed molybdenum compound in an oil solution and arrive at the presently recited stable colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, wherein the stable colloidal suspension is clear” of independent Claims 1, 18 and 43. Accordingly, one skilled in the art would be led away by the disclosure in Price.

In addition, with respect to Claim 18, nowhere does Price provide any suggestion or motivation of a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates, polyvanadates, polyniobates, polytantalates, polyuranates, and mixtures thereof; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 18.

Nor, with respect to Claim 43, does Price provide any suggestion or motivation of a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 43.

Rather, as stated above, Price discloses a colloidal molybdenum complex obtained by extracting a *molybdenum compound* from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and heating and stripping the dispersion with gases to remove the ketone and water from the dispersion. Price further discloses that “[a]fter a period of agitation for

proper contact with the ketone and then a period of settling for separation, the ketone extract layer is added to a suitable dispersant.” Price goes on to state that the ketone and water are thereafter removed. However, by subjecting the mixture of recited components (a)-(c) to agitation, a micro emulsion can be obtained, which, after heating to a temperature to remove sufficient water, produces the claimed stable clear colloidal suspension which is substantially clear. Certainly, then, the disclosure in Price of first agitating the ketone extract layer, adding a dispersant to the ketone extract layer and then removing the ketone and water therefrom to prepare the colloidal molybdenum complex provides no suggestion, motivation or even a hint of forming a micro emulsion by subjecting the mixture of recited components (a)-(c) to agitation and then heating the micro emulsion to a temperature to remove sufficient water and produce the claimed stable clear colloidal suspension which is substantially clear as presently recited in Claims 18 and 43. Accordingly, Claims 18 and 43 are believed to be further patentable over Price.

For the foregoing reasons, Claims 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 are believed to be nonobvious, and therefore patentable, over Price. Accordingly, withdrawal of the rejection of Claims 1-11, 14-23, 26-37, 39, 40, 42-45, 49-51 and 54-62 under 35 U.S.C. §103(a) is respectfully requested.

The Examiner has rejected Claims 1-62 under 35 U.S.C. §103(a) as being obvious over Price in view of Valcho et al. U.S. Patent No. 4,601,837 (“Valcho et al.”). This rejection is respectfully traversed.

The deficiencies of Price discussed above apply with equal force to this rejection.

Valcho et al. do not cure and are not cited as curing the deficiencies of Price. Instead, Valcho et al. are merely cited for the disclosure that polybutene succinic anhydride can be added to the reaction zone as a process aid in the manufacture of an overbased molybdenum-alkaline earth metal sulfonate to increase the efficiency of molybdenum incorporation and improve product clarity. However, as with the disclosure in Price, Valcho et al. likewise provide no suggestion or motivation of a stable colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... *polymolybdates* ... and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, *wherein the stable colloidal suspension is substantially clear*” as generally recited in independent Claims 1, 18 and 43.

Rather, Valcho et al. disclose a process for the manufacture of an *overbased molybdenum-alkaline earth metal sulfonate*. Valcho et al. further disclose that the overbased molybdenum-alkaline earth metal sulfonate product will have a Total Base Number (TBN) of at least 300. Accordingly, by overbasing the molybdenum-alkaline earth metal sulfonate, the pH of the product will necessarily be greater than 7.

However, at a pH of greater than 7, any polymolybdate present in the solution would breakdown into a non-polymeric molybdate. This is again evidenced in Exhibit 1 which states that “In aqueous solution the behavior of Mo(VI) is extremely pH-dependent. Above pH 7 molybdenum (VI) occurs as the tetrahedral oxyanion MoO_4^{2-} , but below pH 7 a complex series of concentration-, temperature-, and pH-dependent equilibria exist. The best known of these equilibria leads to the formation of the heptamolybdate, $\text{Mo}_7\text{O}_{24}^{6-}$... and octamolybdate,

Mo₈O₂₆⁴⁻, ions.” As such, nothing in Valcho et al. would lead one skilled in the art to look to the polybutene succinic anhydride processing aids for the manufacture of an overbased molybdenum-alkaline earth metal sulfonates disclosed therein to modify the colloidal *molybdenum* complex of Price and arrive at the presently recited stable colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... *polymolybdates* ... and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, *wherein the stable colloidal suspension is substantially clear*” of independent Claims 1, 18 and 43. In fact, even by combining Price with Valcho et al. one skilled in the art would not even arrive at the presently claimed stable colloidal suspension.

In addition, with respect to Claim 18, nowhere does Valcho et al provide any suggestion or motivation of a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates, polyvanadates, polyniobates, polytantallates, polyuranates, and mixtures thereof; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 18.

Nor, with respect to Claim 43, does Valcho et al provide any suggestion or motivation of a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in Claim 43.

Rather, as stated above, Valcho et al. simply disclose stirring the reaction mixture to prepare the overbased molybdenum-alkaline earth metal sulfonate. However, stirring alone would be insufficient to form a micro emulsion as presently recited in Claims 18, 43 and 63. This is evidenced in Exhibit 2 (as attached herein) which states that colloid mills are used to emulsify liquids and further states that the colloid mills operate by rotating at speeds of 1,000-20,000 rpm. By subjecting the mixture of recited components (a)-(c) to agitation, a micro emulsion can be obtained, which, after heating to a temperature to remove sufficient water, produces the claimed stable colloidal suspension. Certainly, then, the disclosure in Valcho et al. of simply stirring the reaction mixture to prepare the overbased molybdenum-alkaline earth metal sulfonate provides no suggestion, motivation or even a hint of forming a micro emulsion by subjecting the mixture of recited components (a)-(c) to agitation and then heating the micro emulsion to a temperature to remove sufficient water and produce the claimed stable colloidal suspension as presently recited in Claims 18 and 43. As such, nothing in Valcho et al. would lead one skilled in the art to look to the step of stirring the reaction mixture to prepare the

overbased molybdenum-alkaline earth metal sulfonate disclosed therein to modify the colloidal *molybdenum* complex of Price and arrive at the recited steps of forming a micro emulsion by subjecting the mixture of recited components (a)-(c) to agitation and then heating the micro emulsion to a temperature to remove sufficient water and produce the claimed stable colloidal suspension which is substantially clear as presently recited in Claims 18 and 43. Again, even by combining Price with Valcho et al. one skilled in the art would not even arrive at the presently claimed processes.

Accordingly, Claims 1-62 are believed to be nonobvious, and therefore patentable, over Price in view of Valcho et al. Therefore, withdrawal of the rejection of Claims 1-62 under 35 U.S.C. §103(a) is respectfully requested.

For the foregoing reasons, Claims 1-75 as presented herein are believed to be in condition for allowance. Such early and favorable action is earnestly solicited.

Respectfully submitted,



Michael E. Carmen
Reg. No. 43,533
Attorney for Applicants

M. CARMEN & ASSOCIATES, PLLC
170 Old Country Road – Suite 400
Mineola, NY 11501
Phone: (516) 992-1848
Facsimile: (516) 739-0981
MEC:bg

EXECUTIVE EDITOR
Jacqueline I. Kroschwitz

EDITOR
Mary Howe-Grant

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME 16

MASS TRANSFER
TO
NEUROREGULATORS



A Wiley-Interscience Publication
JOHN WILEY & SONS
New York • Chichester • Brisbane • Toronto • Singapore

CONTENTS

Matches	1	N
Materials Reliability	8	N
Materials Standards and Specifications	33	N
Meat Products	68	N
Medical Diagnostic Reagents	88	N
Medical Imaging Technology	107	M
Membrane Technology	135	M
Memory-Enhancing Drugs	193	M
Mercury	212	M
Mercury Compounds	228	M
Metal Anodes	244	M
Metallic Coatings	258	M
Metallurgy	313	M
Metal-Matrix Composites	392	M
Metal Surface Treatments	416	M
Metal Treatments	449	N
Methacrylic Acid and Derivatives	474	N
Methacrylic Polymers	506	N

This text is printed on acid-free paper.

Copyright © 1995 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012.

Library of Congress Cataloging-in-Publication Data

Encyclopedia of chemical technology/executive editor; Jacqueline I. Kroschwitz; editor, Mary Howe-Grant. —4th ed.

p. cm.

At head of title: Kirk-Othmer.

"A Wiley-Interscience publication."

Includes index.

Contents: v. 16, Mass Transfer to neuroregulators

ISBN 0-471-52685-1 (v. 16)

1. Chemistry, Technical—Encyclopedias. I. Kirk, Raymond E. (Raymond Eller), 1890–1957. II. Othmer, Donald F. (Donald Frederick), 1904–. III. Kroschwitz, Jacqueline I., 1942–.

IV. Howe-Grant, Mary, 1943–. V. Title: Kirk-Othmer encyclopedia of chemical technology.

TP9.F685 1992

660.03—dc20

91-16789

MOLYBDENUM COMPOUNDS

The chemistry of molybdenum, Mo, is among the most diverse of the transition elements. In its compounds, molybdenum exhibits coordination numbers from four to eight, oxidation numbers from -II to VI, and numerous states of aggregation (nuclearity). Molybdenum forms binary compounds with many nonmetallic elements, and a number of these, namely the halides, oxides, sulfides, carbides, nitrides, and silicides, are of technological interest. In contrast to its congeners, chromium and tungsten, molybdenum is found naturally in the form of its sulfide molybdenite [1309-56-4], MoS_2 . Similarly, in the enzymes in which molybdenum is found, the active site Mo is generally in a high sulfur environment. This thio-philicity of Mo also plays a role in a number of its technological uses.

In biology molybdenum is a component of fertilizer and nutrient formulations (see FERTILIZERS; MINERAL NUTRIENTS). Over 20 enzymes have been found to have molybdenum as a component of their active sites. The roles of molybdenum in nitrogen fixation (qv) and nitrate reduction establish this metal as a key element of a biological nitrogen cycle. In technology various solid and soluble molybdenum compounds have found use in lubrication (see LUBRICATION AND LUBRICANTS); hydrodesulfurization, hydrogenation, and oxidation catalysis; anticorrosion and coatings (qv); flame and smoke retardancy (see FLAME RETARDANTS); and various forms of pigmentation.

The most important molybdenum oxidation states are VI, V, IV, III, II, and 0. The higher oxidation states are usually characterized by molybdenum binding to electronegative atoms, such as oxygen and the halogens. The lowest oxidation states are largely in the realm of organometallic chemistry, wherein the Mo is bound directly to the carbon atom of carbon monoxide (qv), to organic phosphines, and/or to a variety of unsaturated carbonaceous ligands.

Molybdenum(VI)

The chemistry of hexavalent molybdenum is very prominent in both biological and industrial systems. Oxygen coordination of molybdenum is most common in this oxidation state (1-3). Molybdenum trioxide [1313-27-5], MoO_3 , is a key intermediate in the technological utilization of molybdenum (Fig. 1). In the refining of Mo, molybdenite ore, MoS_2 , which contains tetravalent Mo, is first roasted in air to form impure MoO_3 . The MoO_3 is then reduced to the metal with hydrogen from 500-1150°C. The trioxide melts at 795°C but sublimes significantly below that temperature. The structure of MoO_3 is a complex, layered arrangement in which each of the six-coordinate Mo(VI) atoms shares the face of an octahedron with another Mo(VI) atom. The MoO_3 reacts with base to produce a variety of molybdate salts, the simplest of which are of the form M_2MoO_4 . Sodium molybdate [7631-95-0] is an example. These water-soluble salts serve as the starting materials for the synthesis of a wide variety of compounds.

The molybdate ion, MoO_4^{2-} , is a d^0 , four-coordinate, tetrahedral anion. The structure (Fig. 2a) resembles that of other Group 6 (VIB) and Group 16 (VIA) ions, such as CrO_4^{2-} , WO_4^{2-} , SO_4^{2-} , and SeO_4^{2-} . The discrete dimolybdate ion [19282-23-6], $\text{Mo}_2\text{O}_7^{2-}$, exists in $\text{N}(\text{C}_4\text{H}_9)_4^+$ salts (see QUATERNARY AMMONIUM

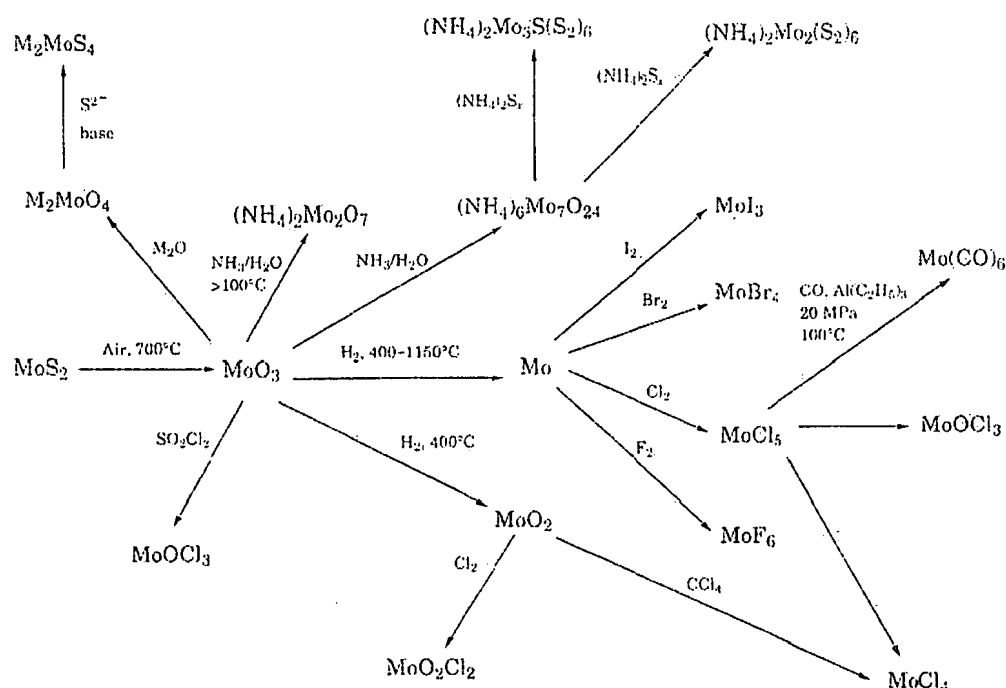


Fig. 1. Scheme for the preparation of technologically important compounds of molybdenum, where M = Li, Na, K, Rb, Cs, and NH₄. To convert MPa to psi, multiply by 1.45.

COMPOUNDS). Diammonium dimolybdate [27546-07-2], (NH₄)₂Mo₂O₇, available commercially as the tetrahydrate and prepared from MoO₃ and excess NH₃ in aqueous solution at 100°C, has an infinite chain structure based on MoO₆ octahedra. In aqueous solution the behavior of Mo(VI) is extremely pH-dependent (4). Above pH 7 molybdenum(VI) occurs as the tetrahedral oxyanion MoO₄²⁻, but below pH 7 a complex series of concentration-, temperature-, and pH-dependent equilibria exist. The best known of these equilibria lead to the formation of the heptamolybdate, Mo₇O₂₄⁶⁻ (Fig. 2h), and octamolybdate, Mo₈O₂₆⁴⁻, ions. Even larger aggregates may be present in solution and in salts. Both Mo₁₂O₃₇²⁻ and Mo₃₆O₁₁₂(H₂O)₁₆⁸⁻ have been isolated and crystallographically characterized (4). At sufficiently low pH in very dilute solutions, cationic forms such as MoO₂²⁺ and MoO⁴⁺ are present.

The polymolybdate and heteropolymolybdate ions constitute a broad and commercially significant class. In these ions molybdenum is six-coordinate with octahedral geometry (4-8). Oxo (O²⁻) groups bridge the Mo atoms and serve as terminal ligands on some of the Mo ions. When other atoms are present during the acidification of molybdate solutions, a series of heteropolymolybdates is formed. For example, cations such as Cr³⁺ or Co²⁺, or anions such as PO₄³⁻ or AsO₄³⁻, form the heteropoly anions H₆CrMo₆O₂₄³⁻, H₆CoMo₆O₂₄⁴⁻, PMo₁₂O₄₀³⁻, and AsMo₁₂O₄₀³⁻, respectively. The yellow ion, PMo₁₂O₄₀³⁻, is analytically useful, being formed in the molybdenum test for phosphate ion. Poly- and heteropolymolybdate ions are used in the precipitation of dyes. The protonated forms of the ions are strongly acidic and many poly- and heteropolymolybdate

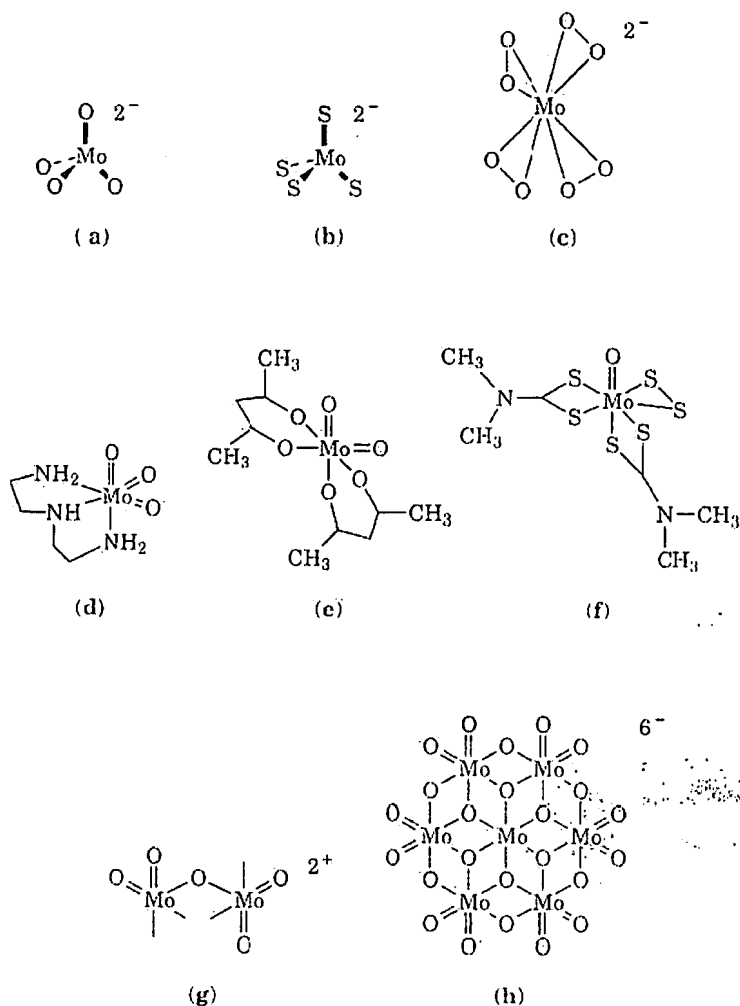


Fig. 2. Representative structures for compounds of molybdenum(VI): (a) molybdate(VI), MoO_4^{2-} ; (b) tetrathiomolybdate(VI), MoS_4^{2-} ; (c) tetrakis(peroxo)molybdate(VI), $\text{Mo}(\text{O}_2)_4^{2-}$; (d) *cis*-trioxodiethylenetriaminemolybdenum(VI), $(\text{MoO}_3(\text{dien}), \text{C}_4\text{H}_{13}\text{N}_3\text{MoO}_3)$; (e) *cis*-bis(acetylacetonato)dioxomolybdenum(VI), $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$; (f) bis(dialkyldithiocarbamato)disulfidooxomolybdenum(VI), $\text{MoO}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2$ (R = alkyl); (g) the dinuclear core structure for $\text{Mo}_2\text{O}_5^{2+}$ complexes; (h) heptamolybdate(VI), $\text{Mo}_7\text{O}_{24}^{6-}$.

compounds have catalytic activity that is attributable to their acid-base or redox properties.

The reduction of molybdate salts in acidic solutions leads to the formation of the molybdenum blues (9). Reductants include dithionite, stannous ion, hydrazine, and ascorbate. The molybdenum blues are mixed-valence compounds where the blue color presumably arises from the intervalence $\text{Mo(V)} \rightarrow \text{Mo(VI)}$ electronic transition. These can be viewed as intermediate members of the class of mixed oxy hydroxides the end members of which are Mo(VI)O_3 and Mo(V)O(OH)_3 [27845-91-6]. MoO_3 and Mo(VI) solutions have been used as effective detectors of reductants because formation of the blue color can

COLLOIDAL SYSTEMS AND INTERFACES

Sydney Ross
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York

Ian Douglas Morrison
Webster Research Center
Xerox Corporation
Webster, New York



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

A NOTE TO THE READER

This book has been electronically reproduced from digital information stored at John Wiley & Sons, Inc. We are pleased that the use of this new technology will enable us to keep works of enduring scholarly value in print as long as there is a reasonable demand for them. The content of this book is identical to previous printings.

Copyright © 1988 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Ross, Sydney, 1915-
Colloidal systems and interfaces/Sydney Ross, Ian Morrison.
p. cm.

"A Wiley-Interscience publication."
Includes bibliographies and index.
ISBN 0-471-82848-3

1. Colloids. 2. Surface chemistry. I. Morrison, Ian.
II. Title.

QD549.R65 1988

541.345--dc19

ISBN 0-471-82848-3

Printed in the United States of America

10 9 8 7 6 5 4 3

87-30529

CIP

A low man got:
His hu
A high man:
M.
BROWNING, /

This book is d
FREDERICK
by two

Processing Methods for Making Emulsions and Suspensions

Processing methods are of two types: those that emulsify or that pull agglomerates apart by shear forces and those that comminute aggregates by fracture. Different equipment is used for each process. Equipment to generate shearing forces need only provide sufficient energy to attenuate an immiscible liquid within another or to separate agglomerates. Comminution requires higher energy input to break tightly bound aggregates or to shatter coherent solids.

The generation of high-shear forces requires narrow gaps, or high rates of flow, or both. The following are examples of equipment in which one or the other of these modes to generate high-shear forces is used. A Banbury mixer, used to blend carbon and other fillers into rubber or plastics, functions at low speed with a loading of high millbase viscosity. The operation of a colloid mill, used to emulsify liquids, depends on flow through a narrow gap. A Kady mill, used to disperse powders in liquids, functions at high speed with a loading of low viscosity (Fig. E.1).

The breaking of aggregates requires impact, which is favored when unhindered by viscous resistance. The fineness of the grind depends on the size of the grinding media: the smaller the media, the finer the grind. Ball or pebble mills are rotated on a shaft or by rollers and the impacts are driven by gravity. Finer media require stirring.

Table E.1 lists high-shear mills in order of increasing viscosity of the millbase and high-impact mills in decreasing order of the size of the grinding media. Appendix K lists the names and addresses of some manufacturers of processing equipment.

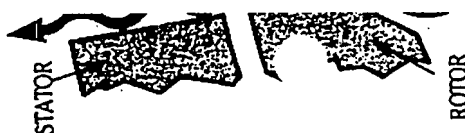
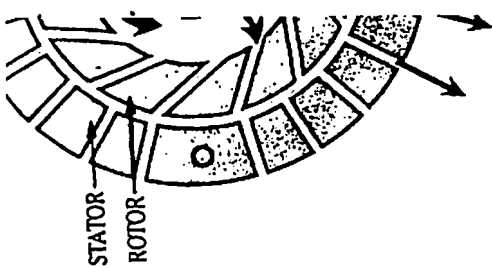


Figure E.1 A Kady mill rotor and stator

CHAPTER IE

Processing Methods for Making Emulsions and Suspensions

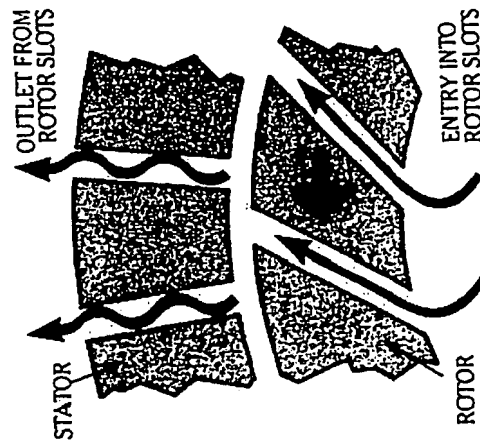
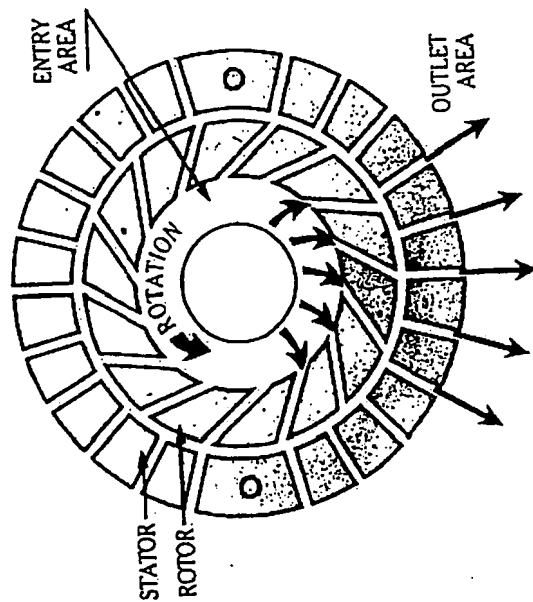


Figure E.1 A Kady mill rotor and stator. (Courtesy of the Kinetic Dispersion Corp.)

processing methods are of two types: those that emulsify or that pull agglomerates apart by shear forces and those that comminute aggregates by fracture. Different equipment is used for each process. Equipment to generate shearing forces need only provide sufficient energy to attenuate an immiscible liquid in another or to separate agglomerates. Comminution requires higher energy input to break tightly bound aggregates or to shatter coherent solids. The generation of high-shear forces requires narrow gaps, or high rates of flow, both. The following are examples of equipment in which one or the other of these modes to generate high-shear forces is used. A Banbury mixer, used to blend ion and other fillers into rubber or plastics, functions at low speed with a lining of high millbase viscosity. The operation of a colloid mill, used to disperse liquids, depends on flow through a narrow gap. A Kady mill, used to disperse powders in liquids, functions at high speed with a loading of low viscosity (E.1).

The breaking of aggregates requires impact, which is favored when unhindered viscous resistance. The fineness of the grind depends on the size of the grinding media: the smaller the media, the finer the grind. Ball or pebble mills are rotated shaft or by rollers and the impacts are driven by gravity. Finer media require grinding.

Table E.1 lists high-shear mills in order of increasing viscosity of the millbase. High-impact mills in decreasing order of the size of the grinding media. Appendix K lists the names and addresses of some manufacturers of processing equipment.

4000-5000 ft/min. Kady mills are contr turning within a labyrinth stator in which excess of 10,000 ft/min.

Colloid mills (Fig. E.2) operate by between a high-speed rotor and a stator. can rotate at speeds of 1,000-20,000 rpm surfaces is adjustable down to a thousar grooved. The liquids are recirculated ar

In the Microfluidizer two streams imp precisely defined microchannels within pressure can be varied from 500 to 20,00 velocities of 1500 ft/s. Fine droplets with by a combination of shear, turbulenc equipment may be used to produce em

VariKinetic dispersers	Ball and pebbic mills
Kady Mills	
Colloid mills.	Attritor
Microfluidizer	
Homogenizer	
Sonolator	
Ultrasonic mills	Sand mills
Three-roll mills	Dyno-Mill
Banbury mixer	

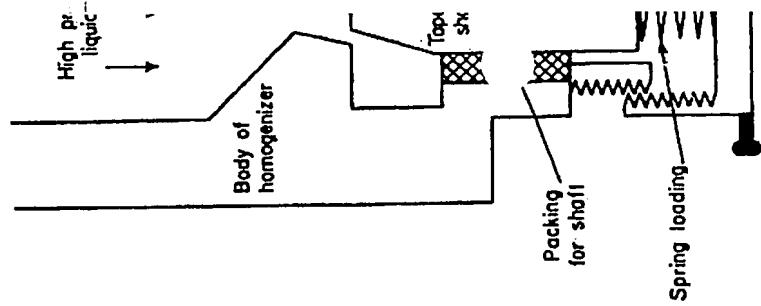


Figure E.3 Section of a single-stage

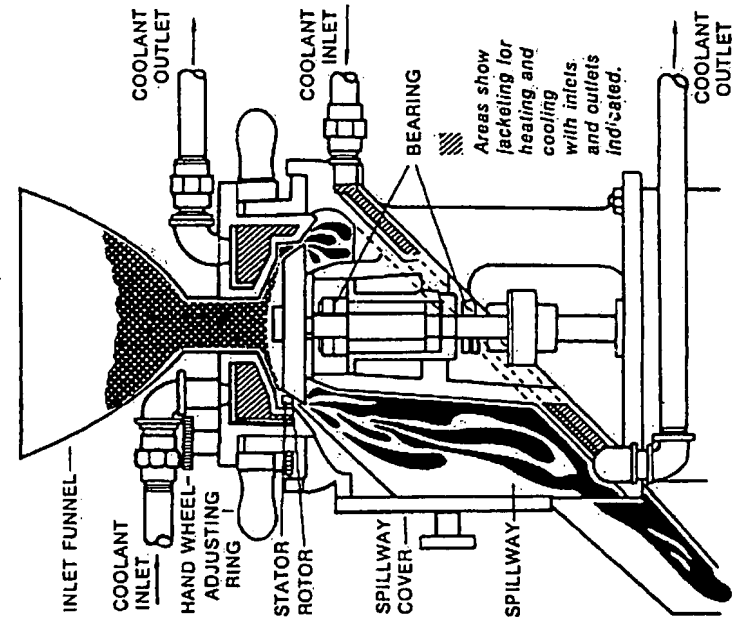


Figure E.2 Section of a vertical colloid mill. (Courtesy of the Premier Mill Corp.)

1. HIGH-SHEAR MILLS

Gaulin's VariKinetic disperser features variable-pitch impeller vanes, the angle of which can be adjusted while the unit is operating. The tip of the vanes moves at 4000–5000 ft/min. Kady mills are continuous mixers using a high-speed rotor turning within a labyrinth stator in which particles are accelerated to velocities in excess of 10,000 ft/min.

Colloid mills (Fig. E.2) operate by sucking liquids through a narrow gap between a high-speed rotor and a stator. The rotor is dynamically balanced and can rotate at speeds of 1,000–20,000 rpm. The gap between the rotor and stator surfaces is adjustable down to a thousandth of an inch. The rotor is sometimes grooved. The liquids are recirculated and the stator is water cooled.

In the Microfluidizer two streams impact at high velocity and high pressure in precisely defined microchannels within the interaction chamber. The process pressure can be varied from 500 to 20,000 psi; the process stream accelerated to velocities of 1500 ft/s. Fine droplets with a narrow size distribution are produced by a combination of shear, turbulence, impact, and cavitation forces. The equipment may be used to produce emulsions, suspensions, and foams.

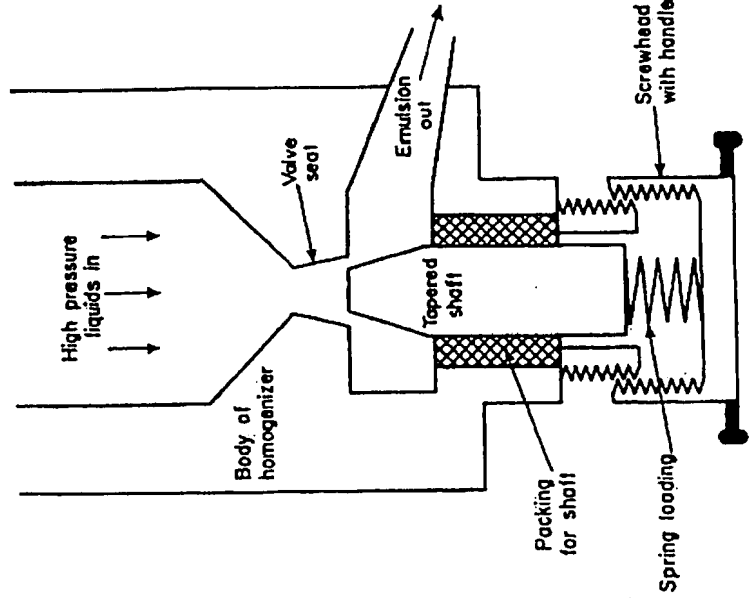


Figure E.3 Section of a single-stage homogenizer (Sherman, 1968, p. 11).

Table E.1 Classification of Milling Equipment

High-Shear Mills (creasing viscosity)	High-Impact Mills (decreasing media size)
VariKinetic dispersers	Ball and pebble mills
Colloid mills	Attritor
Microfluidizer	
Homogenizer	
Rollator	
Grasson mills	
Re-roll mills	Sand mills
	Dyno-Mill
Imbury mixer	

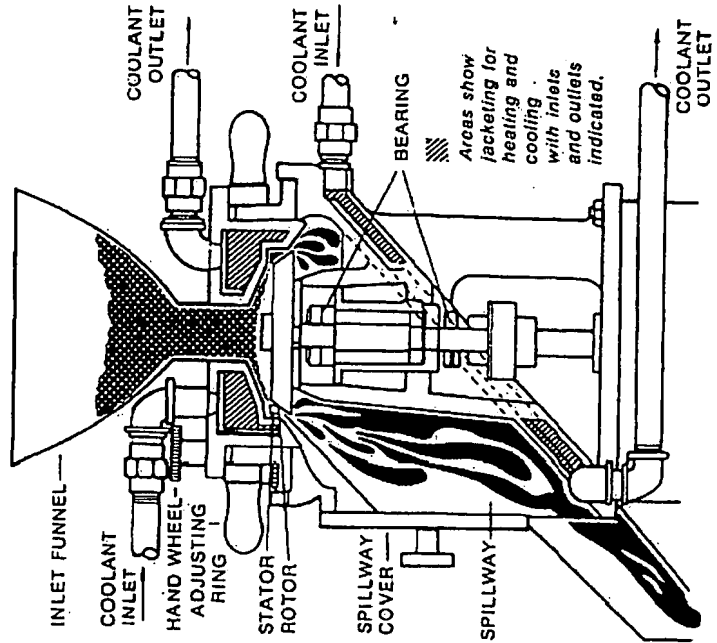


Figure E.2 Section of a vertical colloid mill. (Courtesy of the Premier Mill Corp.)

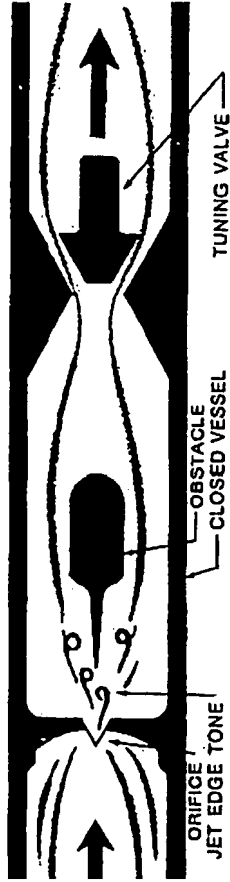


Figure E.4 Schematic diagram of the Sonolator. (Courtesy of the Sonic Corp.)

Homogenizers produce emulsions by forcing the mixture at high pressure (up to 2,000 psi) through a small orifice against a spring-loaded plunger (Figure E.3). The velocity of the liquid through a small gap creates high-shear forces. The lack of moving parts makes it preferable to the colloid mill. A familiar application is to use the size of fat globules in milk.

A Sonolator is a variation of the homogenizer (Figure E.4). A jet of liquid at pressures between 200 and 2000 psi is pumped through an orifice against a delicate obstacle in the jet stream. The turbulent flow of the liquid causes the liquid to resonate at ultrasonic frequencies. A high level of cavitation, turbulence, and shear is the result. The Sonolator can be tuned while in operation to a peak of acoustic intensity.

Ultrasonic activators convert conventional 60-Hz line frequency to 20,000 Hz. High frequency is fed to an electrostrictive element, which converts the signal into mechanical vibrations in tips of various shapes called horns. The tip of the horn is immersed in the liquid in which the ultrasonic vibrations cause cavitation. The horns are primarily laboratory instruments. For continuous use the vibrating horns must be cooled.

A three-roll mill is a set of rolls rotating in opposite directions with a small clearance between the rolls. High-shearing action is exerted on the agglomerate, forcing it to break up. High viscosity of the loading is important for this type of operation; therefore, percent solids is kept as high as possible. Its advantages are that it handles viscous materials such as printing inks. The disadvantage is that it is open to the air and so cannot be used with volatile solvents.

In the Banbury mixer or mill two kneading arms or rotors are encased in a mixing chamber that rotates in opposite directions and at different speeds. They are so shaped that the plastic mixture is pressed against the walls of the chamber, forming a wedge during the kneading operation. The wedge is continuously formed and moved, while the motion of the rotors ensures good mixing of the batch. The chamber is heated to mill polymers above their glass transition temperatures.

2. IMPACT MILLS

Micronizer is a dry-process machine in which particles are fluidized in two crossed streams of air from high-speed jet nozzles, which project particles against each other at high kinetic energies. The nozzles are precisely aimed—within

fractions of a second in degrees of arc. The carrier fluid pressure and feed materials are equivalent on both sides. The mixture is classified by being blown into a vortex. The smaller particles follow the streamlines of the air and exit with it; the larger particles are recirculated until ground small enough to escape. The equipment is well suited to break up soft solids such as carbon blacks, molybdenum disulfide, and polymers.

A ball mill is any rolling mill in which steel or iron balls are used as the grinding medium (Fig. E.5). The cylinder is usually made of steel. A pebble mill uses flint

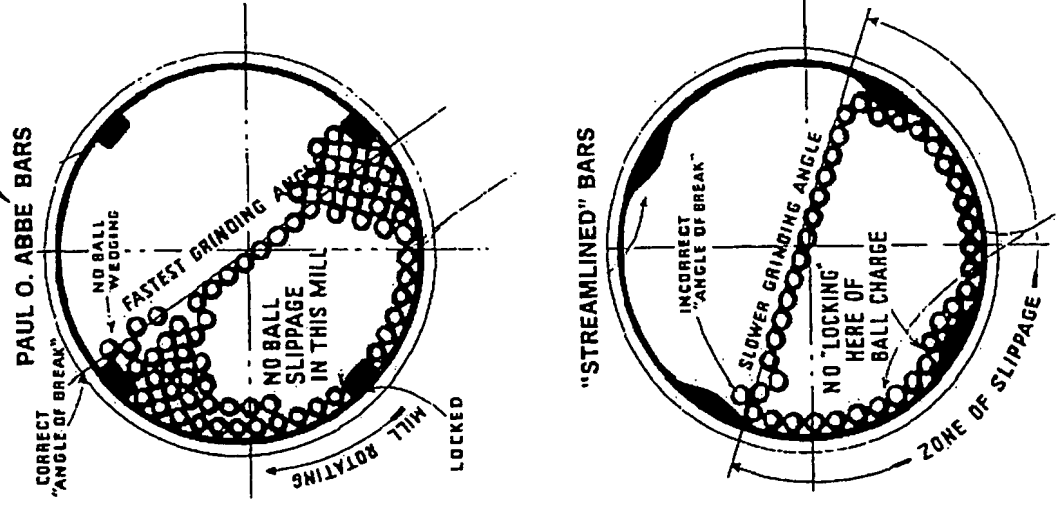


Figure E.5 Milling action in a ball mill. (Courtesy of Paul O. Abbe, Inc.)